CLAIMS

What is claimed as our invention is:

1. A method comprising:

contacting an oligomerization catalyst system and a feed comprising olefins;

oligomerizing said feed in at least one continuous reactor; and

withdrawing from said at least one continuous reactor an effluent comprising product olefins having at least four carbon atoms;

wherein the oligomerization catalyst system comprises iron or cobalt, or combinations thereof; and

wherein oligomerization to product olefins having at least four carbon atoms comprises a single pass conversion of ethylene of at least about 40 weight percent.

- 2. The method of Claim 1, wherein the single pass conversion of ethylene is at least about 65 weight percent.
- 3. The method of Claim 1, wherein product olefins having twelve carbon atoms comprise at least about 95 weight percent 1-dodecene.
- 4. The method of Claim 1, wherein the effluent comprises at least about 40 weight percent product olefins having at least four carbon atoms.

- 5. The method of Claim 1, wherein said product olefins comprise at least about 80 weight percent linear 1-alkenes.
- 6. The method of Claim 1, wherein said product olefins comprise at least about 20 weight percent alpha olefins having from about 8 to about 20 carbon atoms.
- 7. The method of Claim 1, wherein said oligomerization catalyst system comprises a metal alkyl or metal hydride species.
- 8. The method of Claim 7, wherein said metal alkyl or metal hydride species comprises one or more Lewis acids; a combination of one or more Lewis acids and one or more alkylating agents; one or more alkyl aluminum compounds; one or more alkyl aluminoxanes; methyl aluminoxane (MAO); modified MAO; tri-alkyl aluminum; diethylaluminum chloride (DEAC); or combinations thereof.
- 9. The method of Claim 1, wherein said oligomerization catalyst system comprises triethylaluminum (TEA), trimethylaluminum (TMA), tri-isobutyl aluminum (TIBA), tri-butyl aluminum, or combinations thereof.
- 10. The method of Claim 1, wherein the oligomerization catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure I:

$$R^1$$
 R^4
 R^6
 R^6
 R^2
 R^3
 R^5
 R^7

I

wherein R¹, R², and R³ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, or any two of R¹-R³, vicinal to one another, taken together may form a ring;

R⁴ and R⁵ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or inert functional group; and

 R^6 and R^7 may be identical or different, and are independently aryl, substituted aryl, optionally substituted heterohydrocarbyl moiety, optionally substituted aryl group in combination with and Π -coordinated to a metal, optionally substituted aromatic hydrocarbon ring, or optionally substituted polyaromatic hydrocarbon moiety.

11. The method of Claim 1, wherein said oligomerization catalyst system is activated in the absence of ethylene.

- 12. The method of Claim 10, further comprising selecting R¹-R⁷ such that said metal complex is symmetrical.
- 13. The method of Claim 10, further comprising selecting R¹-R⁷ such that said metal complex is asymmetrical.
- 14. The method of Claim 1, wherein said oligomerization catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure II:

wherein R_1 , R_2 , and R_3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

 R_4 and R_5 are each independently hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl; and

Y is a structural bridge, and W, Y, and Z independently comprise hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl having from about 0 to about 30 carbon atoms.

15. The method of Claim 1, wherein said oligomerization catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure III:

$$R_4$$
 R_2
 R_3
 R_5
 R_5
 R_5

Ш

wherein R_1 - R_5 each comprise, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1 - R_3 vicinal to one another taken together may form a ring;

 Z_1 , which is different from Z_2 , is an aryl or substituted aryl group; and

 Z_2 comprises an aryl, substituted aryl, optionally substituted heterohydrocarbyl moiety, or an optionally substituted aryl group in combination with and Π -coordinated to a metal.

- 16. The method of Claim 15, wherein Z_2 is an aryl, substituted aryl, optionally substituted aromatic heterocyclic moiety, an optionally substituted polyaromatic heterocyclic moiety, an optionally substituted aliphatic heterocyclic moiety, or an optionally substituted aliphatic heterohydrocarbyl moiety.
- 17. The method of Claim 1, wherein said oligomerization catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure IV:

wherein A_1 - A_6 each comprise, independently, carbon, nitrogen, oxygen, or sulphur;

 A_1 may be directly bonded to A_5 ;

 R_{1} - R_{12} , R_{14} - R_{15} , and, if present, R_{13} , are each, independently, hydrogen, optionally substituted hydrocarbyl, or an inert functional group;

any two of R_1 - R_{15} , vicinal to one another, taken together may form a ring; and conditionally, when A_1 - A_5 and A_6 , if present, are all carbon, said atoms constitute the cyclopentadienyl or aryl part of a Π -coordinated metal.

18. The method of Claim 1, wherein said oligomerization catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure VI:

$$R_{2}$$
 R_{3}
 R_{6}
 R_{10}
 R_{11}
 R_{12}
 R_{13}

wherein R_1 - R_5 and R_7 - R_9 and R_{12} - R_{14} are each, independently, hydrogen, substituted hydrocarbyl, an inert functional group, or any two of R_1 - R_3 , R_7 - R_9 , and R_{12} - R_{14} , vicinal to one another, taken together may form a ring; and

VI

 R_6 , R_{10} , R_{11} , and R_{15} are identical and are selected from fluorine or chlorine.

19. The method of Claim 1, wherein said oligomerization catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure VII:

VII

wherein R_1 - R_5 and R_7 - R_9 and R_{12} - R_{14} are each, independently, hydrogen, substituted hydrocarbyl, an inert functional group, or any two of R_1 - R_3 , R_7 - R_9 , and R_{12} - R_{14} , vicinal to one another, taken together may form a ring;

R₆ is hydrogen, substituted hydrocarbyl, an inert functional group, or taken together with R₇ or R₄ to form a ring;

 R_{10} is hydrogen, substituted hydrocarbyl, an inert functional group, or taken together with R_9 or R_4 to form a ring; and

 R_{11} and R_{15} are, independently, hydrogen or an inert functional group.

- 20. The method of Claim 1, wherein said oligomerization catalyst system comprises a selective 1-hexene (S1H) catalyst.
- 21. The method of Claim 20, wherein said oligomerization catalyst system comprises chromium.
- 22. The method of Claim 1, wherein said at least one continuous reactor comprises a loop reactor, tubular reactor, continuous stirred tank reactor, or combinations thereof.
- 23. The method of Claim 1, wherein said at least one continuous reactor comprises a loop reactor and fluid flow in said loop reactor comprises a Reynolds number of from about 200,000 to about 700,000.
- 24. The method of Claim 1, wherein said at least one continuous reactor comprises a tubular reactor and fluid flow in said tubular reactor comprises a Reynolds number of from about 300,000 to about 2,000,000.

- 25. The method of Claim 1, wherein at steady state the contents of said reactor are not turbid.
- 26. The method of Claim 1, wherein the effluent comprises a diluent and wherein said diluent comprising aliphatics, non-aliphatics, aromatics, saturated compounds having from 4 to 8 carbon atoms, or combinations thereof.
- 27. The method of Claim 1, wherein the effluent comprises a diluent and wherein said diluent comprises an aromatic compound having from about 6 to about 30 carbon atoms, or combinations thereof.
- 28. The method of Claim 1, wherein the effluent comprises a diluent and wherein said diluent comprises cyclohexane, benzene, toluene, xylene, ethylbenzene, or combinations thereof.
- 29. The method of Claim 1, wherein the effluent comprises a diluent and wherein said diluent comprises olefins having from about 4 to about 30 carbon atoms, or combinations thereof.
- 30. The method of Claim 1, wherein the effluent comprises a diluent and wherein said diluent comprises 1-butene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, or combinations thereof.

- 31. The method of Claim 1, further comprising manipulating product olefin distribution by modifying a pressure of the reactor.
- 32. The method of Claim 1, further comprising injecting said feed and said catalyst system into said reactor at more than one point along the length of said reactor wherein said reactor is a tubular reactor.
- 33. The method of Claim 1, further comprising cooling said reactor with a coolant more volatile than water.
- 34. The method of Claim 1, further comprising cooling said reactor with a coolant, wherein said coolant comprises butane, isobutane, isopentane, or combinations thereof.
- 35. The method of Claim 1, wherein said reactor comprises a temperature of from about 40 to about 150 degrees Celsius.
- 36. A method comprising:

contacting an oligomerization catalyst system and a feed comprising olefins;

oligomerizing said feed in at least one continuous reactor; and

withdrawing from said at least one continuous reactor an effluent comprising product olefins having at least four carbon atoms;

wherein oligomerization to product olefins having at least four carbon atoms comprises a single pass conversion of ethylene of at least about 65 weight percent; and

wherein product olefins having twelve carbon atoms comprise at least about 95 weight percent 1-dodecene.

37. The method of Claim 36, wherein the catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure I:

$$R^{1}$$
 R^{2}
 R^{3}
 R^{5}
 R^{7}

Ι

wherein R¹, R², and R³ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, or any two of R¹-R³, vicinal to one another, taken together may form a ring;

 R^4 and R^5 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or inert functional group; and

 R^6 and R^7 may be identical or different, and are independently aryl, substituted aryl, optionally substituted heterohydrocarbyl moiety, optionally substituted aryl group in combination with and Π -coordinated to a metal, optionally substituted aromatic hydrocarbon ring, or optionally substituted polyaromatic hydrocarbon moiety.

- 38. The method of Claim 37, further comprising selecting R¹-R⁷ such that said metal complex is symmetrical.
- 39. The method of Claim 37, further comprising selecting R¹-R⁷ such that said metal complex is asymmetrical.
- 40. The method of Claim 36, wherein the catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure II:

$$R_{3}$$
 R_{2}
 R_{1}
 R_{4}
 R_{5}
 R_{1}
 R_{4}
 R_{5}
 R_{1}
 R_{2}
 R_{4}
 R_{4}
 R_{5}
 R_{5}
 R_{5}
 R_{5}
 R_{6}
 R_{1}
 R_{2}

II

wherein R_1 , R_2 , and R_3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

 R_4 and R_5 are each independently hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl; and

Y is a structural bridge, and W, Y, and Z independently comprise hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl having from about 0 to about 30 carbon atoms.

41. The method of Claim 36, wherein the catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure III:

$$R_{4}$$
 R_{2}
 R_{3}
 R_{5}
 R_{5}

III

wherein R_1 - R_5 each comprise, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1 - R_3 vicinal to one another taken together may form a ring;

 Z_1 , which is different from Z_2 , is an aryl or substituted aryl group; and

 Z_2 comprises an aryl, substituted aryl, optionally substituted heterohydrocarbyl moiety, or an optionally substituted aryl group in combination with and Π -coordinated to a metal.

- 42. The method of Claim 41, wherein Z_2 is an aryl, substituted aryl, optionally substituted aromatic heterocyclic moiety, an optionally substituted polyaromatic heterocyclic moiety, an optionally substituted aliphatic heterocyclic moiety, or an optionally substituted aliphatic heterohydrocarbyl moiety.
- 43. The method of Claim 36, wherein the catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure IV:

IV

wherein A_1 - A_6 each comprise, independently, carbon, nitrogen, oxygen, or sulphur;

A₁ may be directly bonded to A₅;

R₁-R₁₂, R₁₄-R₁₅, and, if present, R₁₃, are each, independently, hydrogen, optionally substituted hydrocarbyl, or an inert functional group;

any two of R_1 - R_{15} , vicinal to one another, taken together may form a ring; and conditionally, when A_1 - A_5 and A_6 , if present, are all carbon, said atoms constitute the cyclopentadienyl or aryl part of a Π -coordinated metal.

44. The method of Claim 36, wherein the catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure VI:

$$R_{2}$$
 R_{3}
 R_{6}
 R_{10}
 R_{11}
 R_{12}
 R_{13}
 R_{12}
 R_{13}

wherein R_1 - R_5 and R_7 - R_9 and R_{12} - R_{14} are each, independently, hydrogen, substituted hydrocarbyl, an inert functional group, or any two of R_1 - R_3 , R_7 - R_9 , and R_{12} - R_{14} , vicinal to one another, taken together may form a ring; and

R₆, R₁₀, R₁₁, and R₁₅ are identical and are selected from fluorine or chlorine.

45. The method of Claim 36, wherein the catalyst system comprises a metal complex activated by a co-catalyst and wherein said metal complex comprises a ligand having chemical structure VII:

$$R_{10}$$
 R_{10}
 R_{11}
 R_{12}
 R_{13}

VII

wherein R_1 - R_5 and R_7 - R_9 and R_{12} - R_{14} are each, independently, hydrogen, substituted hydrocarbyl, an inert functional group, or any two of R_1 - R_3 , R_7 - R_9 , and R_{12} - R_{14} , vicinal to one another, taken together may form a ring;

 R_6 is hydrogen, substituted hydrocarbyl, an inert functional group, or taken together with R_7 or R_4 to form a ring;

 R_{10} is hydrogen, substituted hydrocarbyl, an inert functional group, or taken together with R_9 or R_4 to form a ring; and

 R_{11} and R_{15} are, independently, hydrogen or an inert functional group.

46. The method of Claim 36, wherein the effluent comprises at least about 40 weight percent product olefins having at least four carbon atoms.

- 47. The method of Claim 36, wherein said product olefins comprise at least about 80 weight percent linear 1-alkenes.
- 48. The method of Claim 36, wherein said product olefins comprise at least about 20 weight percent alpha olefins having from about 8 to about 20 carbon atoms.
- 49. The method of Claim 36, wherein said oligomerization catalyst system comprises a metal alkyl or metal hydride species.
- 50. The method of Claim 49, wherein said metal alkyl or metal hydride species comprises one or more Lewis acids; a combination of one or more Lewis acids and one or more alkylating agents; one or more alkyl aluminum compounds; one or more alkyl aluminoxanes; methyl aluminoxane (MAO); modified MAO; tri-alkyl aluminum; diethylaluminum chloride (DEAC); or combinations thereof.
- 51. The method of Claim 36, wherein said oligomerization catalyst system eo-eatalyst comprises triethylaluminum (TEA), trimethylaluminum (TMA), Tri-isobutyl Aluminum (TIBA), Tri-butyl Aluminum, or combinations thereof.
- 52. The method of Claim 36, wherein the effluent comprises a diluent and wherein said diluent comprises an aromatic compound having from about 6 to about 30 carbon atoms, or combinations thereof.

- 53. The method of Claim 36, wherein the effluent comprises a diluent and wherein said diluent comprises cyclohexane, benzene, toluene, xylene, ethylbenzene, or combinations thereof.
- 54. The method of Claim 36, wherein the effluent comprises a diluent and wherein said diluent comprises olefins having from about 4 to about 30 carbon atoms, or combinations thereof.
- 55. The method of Claim 36, wherein the effluent comprises a diluent and wherein said diluent comprises 1-butene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, or combinations thereof.
- 56. The method of Claim 36, further comprising manipulating product olefin distribution by modifying a pressure of the reactor.
- 57. The method of Claim 36, further comprising injecting said feed and said catalyst system into said reactor at more than one point along the length of said reactor wherein said reactor is a tubular reactor.
- 58. The method of Claim 36, further comprising cooling said reactor with a coolant more volatile than water.

- 59. The method of Claim 36, further comprising cooling said reactor with a coolant, wherein said coolant comprises butane, isobutane, isopentane, or combinations thereof.
- 60. The method of Claim 36, wherein said reactor comprises a temperature of from about 40 to about 150 degrees Celsius.
- 61. The method of Claim 36, wherein said catalyst system comprises a transition metal.
- 62. The method of Claim 36, wherein said catalyst system comprises iron or cobalt, or combinations thereof.
- 63. The method of Claim 36, wherein said catalyst system comprises nickel.
- 64. The method of Claim 36, wherein said reactor comprises a loop reactor, tubular reactor, continuous stirred tank reactor, or combinations thereof.
- 65. The method of Claim 36, wherein said at least one continuous reactor comprises a loop reactor and fluid flow in said loop reactor comprises a Reynolds number of from about 200,000 to about 700,000.

- 66. The method of Claim 36, wherein said at least one continuous reactor comprises a tubular reactor and fluid flow in said tubular reactor comprises a Reynolds number of from about 300,000 to about 2,000,000.
- 67. The method of Claim 36, wherein at steady state the contents of said reactor are not turbid.
- 68. A method of oligomerizing alpha olefins comprising contacting a metal complex having chemical structure VIII with a co-catalyst and a feed comprising olefins:

wherein R_1 , R_2 , and R_3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

 R_4 and R_5 are each independently hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl;

Y is a structural bridge, and W, Y, and Z are independently hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl having from about 0 to about 30 carbon atoms;

wherein M_1 and M_2 are metal atoms that are independently selected from a group comprising cobalt, iron, chromium, and vanadium;

each X is an anion; and

n is 1, 2, or 3, so that the total number of negative charges on X is equal to the oxidation state of M_1 or M_2 .

69. The method of Claim 68, further comprising:

withdrawing from a continuous reactor an effluent comprising at least about 25 weight percent product olefins having at least four carbon atoms.

70. The method of Claim 68, further comprising:

withdrawing from a continuous reactor an effluent comprising at least about 40 weight percent product olefins having at least four carbon atoms.

71. The method of Claim 68, further comprising:

withdrawing from a continuous reactor an effluent comprising product olefins having twelve carbon atoms wherein said product olefins having twelve carbon atoms comprise at least about 95 weight percent 1-dodecene.

72. The method of Claim 68, further comprising:

withdrawing product olefins from a continuous reactor wherein said product olefins comprise at least about 20 weight percent alpha olefins having from about 8 to about 20 carbon atoms.

73. The method of Claim 68, further comprising:

withdrawing product olefins from a continuous reactor wherein said product olefins comprise from about 20 to about 80 weight percent olefins having 6 carbon atoms and wherein said product olefins comprise at least about 20 weight percent olefins having greater than 6 carbon atoms.

74. The method of Claim 68, further comprising:

withdrawing from a continuous reactor product olefins comprising olefins having six carbon atoms wherein said olefins having six carbon atoms comprise at least about 98 weight percent 1-hexene.

- 75. An alpha olefin prepared according to the method of claim 1.
- 76. An alpha olefin prepared according to the method of claim 36.